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COMPLETE SPECIFICATION

Improvements in or relating to Spectrometry

I, MARCEL JULES EDOUARD GOLAY, a citizen of the United States of America, of 372, Hollywood Avenue, West End, New Jersey, United States of America, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement :—

This invention relates to spectrometry and more particularly to infra-red spectrophotometry.

This invention has for an object to provide a spectrophotometer with a high signal-to-noise ratio, and it consists in a spectrometer comprising a number of entrance slits for respectively admitting a corresponding number of beans of the radiation to be examined, means for spectrally dispersing all said beams of light, an equal number of exit slits, means for reconverging said spectrally dispersed beams into dispersed spectra and projecting radiation of the selected wavelength from each inlet slit through one of said exit slits, whereby the exit slits are respectively co-ordinated to the individual inlet slits, pulse-coding means associated with each inlet slit for distinctively pulse-coding each of said beams, beam-transit-control means associated with each exit slit, said beam control means being pulse-coded in such manner at each exit slit as to permit radiation bearing the pulse code of the corresponding inlet slit to pass at pre-determined on-periods while opposing the passage of such radiation during the inter-lying off-periods, and to allow radiation bearing the pulse code of any other inlet slit to pass in equal amounts in the on and off periods, and means for measuring the difference of the total radiation passing through the exit slits in the on and off periods respectively.

It should be understood that even during the on periods the amount of radiation passing through a pair of associated entrance and exit slits will, due to the coding, normally be reduced in comparison with the amount that would pass in the absence of coding, and more particularly that normally the passage of such radiation will only be permitted during a predetermined part of each on period.

Preferably, the spectrometer comprises means for periodically interrupting at different rates and/or phases the beams passing respectively through the various inlet slits and co-ordinated means for periodically interrupting the passage of radiation through the various exit slits at different rates and/or phases respectively.

The attached drawings illustrate one practical embodiment of the invention :

Fig. 1 is a diagrammatic view shown in section and blocks illustrating the general arrangement of the spectrophotometer of my invention ;

Fig. 2 is a front elevation of a scanning disc used in the spectrophotometer of Fig. 1 ; and

Fig. 3 is a front elevation of another scanning disc used in the spectrophotometer of Fig. 1.

The invention will be described, by way of example, with reference to an infra-red spectrophotometer. In order to increase the radiation analyzed while maintaining the resolving power of the spectrophotometer, the entrance and exit apertures are made wider than hitherto customary, so as to admit more radiation and thereby increase the radiative output, and in order to permit this to be done without sacrificing the resolving power the widened entrance and exit apertures are subdivided into a number of slits, and the beams of radiation passing through the individual entrance slits are subjected to distinctive pulse-coding modulations, and complementary decoding means are associated with the individual exit slits in order that only radiation passing through co-ordinated entrance and exit slits is measured by the detector.

The pulse coding and decoding can be obtained by various means. One such

means is an "on" and "off" blocking of the entrance and exit slits in the spectrum to pass the unwanted radiations at a uniform intensity while passing and blocking alternately the wanted radiations. At the same time a definite signal is obtained to mark the "on" and "off" periods of the wanted radiations and this definite signal is utilised to transform the signal fluctuations registered by the detector and amplified in the associated circuits into a direct electrical output current which provides a measure of said wanted radiation.

In Fig. 1 a spectrophotometer is shown incorporating a monochromator 10 according to this invention. Radiation, and more particularly infra-red radiation, emanating from a source 11, which may be a Nernst lamp or other suitable device, produces a beam 12 which, after reflection by a flat mirror 13 and by a concave mirror 14, produces an image of source 11 which substantially fills an entrance aperture 17. The radiation passed by aperture 17 is collimated by a second concave mirror 20, dispersed by prism 19, reflected by Littrow mirror 21, dispersed a second time by prism 19 and converged by mirror 20 to an exit aperture 18 after reflection by flat mirror 22. The emerging beam is reflected by mirror 23 and re-converged by concave lens 24 on a detector 26 which may be a thermopile, or a bolometer, or a photocell, or any other suitable detector of radiant energy which yields an electrical output, which, after passing through an amplifier-rectifier 31, is conducted by leads 32 to a suitable recorder.

To effect the "on" and "off" modulation of the wanted radiation while maintaining the unwanted radiations at a substantially constant level, entrance and exit apertures 17 and 18 are subdivided into a number of slits, and as shown and described herein, for the sake of illustration, the apertures 17 and 18 include six slits. Furthermore the monochromator is provided with two synchronously rotating opaque discs 27 and 28, the outer portions of which are adjacent to entrance and exit apertures 17 and 18 respectively and are provided with slots 48 and 49 respectively to permit transmission of radiation. Figs. 2 and 3 illustrate the slot arrangement of said discs and their positions with respect to the six slits constituting the entrance and exit apertures 17 and 18. Fig. 2 shows the disc 27 as viewed from the left-hand end of spectrometer 10 as shown in Fig. 1, and Fig. 3 shows disc 28 as viewed from the top of the drawing to the bottom of the drawing as shown in Fig. 1. In Fig. 2 the six entrance slits of the entrance aperture 17 are shown, partly in dotted line, behind the disc 27 and are numbered 41 to 46 respectively. In Fig. 3 the exit slit member 18 and its six slits 51 to 56 are shown, partly in dotted outline. The slots 48 and 49 are formed in six discontinuous circles having the axes of rotation 40 and 50 respectively of the discs 27 and 28 as a centre, in each of the discs 27 and 28, adjacent to the six slits in each of the entrance and exit apertures 17 and 18. The six entrance slits 41 to 46 and the six exit slits 51 to 56 are so positioned with respect to each other and to the optics of the monochromator that when the portion of the spectrum which it is desired to study, which portion is also designated as wanted radiation, enters through slit 41 and egresses through slit 51, the same portion of the spectrum will enter through slit 42 and egress through slit 52, and pairs of slits 43 and 53, 44 and 54, 45 and 55, and 46 and 56, will likewise be corresponding slits for the desired portion of the spectrum.

The pulse-coding of the radiation passing through the monochromator 10 is effected by synchronously rotating discs 27 and 28. The complete period of rotation of the discs 27 and 28 is divided for the purposes of this description into eight time intervals characterized by eight sections marked I to VIII in anticlockwise and clockwise direction respectively around the discs 27 and 28. Time intervals I to IV will be referred to as the first half-period, and time intervals V to VIII will be referred to as the second half-period.

From the arrangement of the slits 41 to 46 and slots 48 illustrated in Fig. 2, it will be seen that the wanted radiation which passes in through the centre of slit 41 and out through slit 51, will be blocked during the first half-period either by disc 27 or by disc 28, whereas it will be allowed to pass during intervals VI and VIII when slits 41 and 51 are simultaneously uncovered by slots 48 and 49. Likewise, the passage of the wanted radiation through all the centres of the pairs of corresponding slits will be blocked by one or the other disc during the first half-period whereas the passage of the wanted radiations will be allowed for two of the four time intervals in the second half-period. On the other hand, it will be seen that an unwanted portion of the spectrum passing through the centre of entrance slit 41 and out through the centre of exit slit 54 will be blocked at all times, and likewise the unwanted radiations passing through entrance and exit slits 42 and 55, 43 and 56, 44 and 51, 45 and 52, and 46 and 53, respectively, will be blocked at all times. Further, the passage of unwanted radiation in and out through the centres of any other non-corresponding pairs of slits will be allowed during one of the four time intervals of each half period and blocked during the other time intervals. Summarising, the wanted radiation is blocked during the first half

period and is permitted to pass through all of the corresponding pairs of slits for two out of four of the intervals in the second half period, whereas unwanted radiation is blocked from passing at any time through six of the non-corresponding pairs of entrance and exit slits and is permitted to pass through the other non-corresponding pairs of slits one out of the four time intervals in each of the half periods. Consequently, the wanted radiation is concentrated in the second half-period whereas the unwanted radiation is distributed in equal amounts in both half-periods, and during the second half-period the six slits in combination will pass the wanted radiation in a total amount which is three times larger than if only one slit of the same width had been used.

The radiation passing through the exit slits and focused on the detector is detected by the detector 26 and the amplifier-rectifier combination 31, which, for the embodiment just described, must have a small build-up time constant when compared to the period of rotation of the discs, as well as a long decay time constant when compared to the same period. The amplified voltage derived from the amplifier is rectified in synchronism with the " on " and " off " half-periods of the wanted radiation in the sense that it produces a direct current which is a measure of the excess of radiative energy reaching the detector during the " off " half-period. The electronic processes employed for this purpose are well-known in the art, and it will be readily realized that the electrical measure thus obtained represents only the wanted radiation, since the amounts of unwanted radiative energy reaching the detector during the " on " half-period and during the " off " half-period are equal. The synchronizing signals needed for performing this synchronous rectification are generated by a photocell 37, which is excited during one half-period by the radiation 35 from a source 36, while during the other half-period the radiation 35 from the source 36 is blocked from the photocell 37 by a chopping disc 34 which rotates synchronously with discs 27 and 28.

The determination of the arrangement of the patterns of slots 48 and 49 in the discs 27 and 28 will be best understood by assuming the circles are straightened into horizontal columns of ones (1) and zeros (0) in which the numbers " 1 " represent the light-transmitting slots for a single time interval and the numbers " 0 " represent the opaque section for a single time interval. Accordingly the patterns of the two complementary discs 27 and 28 illustrated by Figs. 2 and 3 will be represented by the two following rectangular patterns, in which the left half represents the first half-period, during which the wanted radiation is " [illegible] and the right half represents the second half-period, during which the wanted radiation is " on " half of the time.

CHART I
Disc 27

Intervals	I	II	III	IV	V	VI	VII	VIII
Slit 41	0	1	0	1	0	1	0	1
42	0	0	1	1	0	0	1	1
43	0	1	1	0	0	1	1	0
44	0	1	0	1	1	0	1	0
45	0	0	1	1	1	1	0	0
46	0	1	1	0	1	0	0	1

CHART II
Disc 28

Intervals	I	II	III	IV	V	VI	VII	VIII
Slit 51	1	0	1	0	0	1	0	1
52	1	1	0	0	0	0	1	1
53	1	0	0	1	0	1	1	0
54	1	0	1	0	1	0	1	0
55	1	1	0	0	1	1	0	0
56	1	0	0	1	1	0	0	1

The time intervals are indicated horizontally across the page whereas the slits are presented vertically. The passage or non-passage of the wanted and unwanted radiation may be determined from the study of the successive columns of the first pattern and of the corresponding columns of the second pattern. Patterns of similar effect for greater or smaller numbers of slots may be obtained arithmetically as follows. Consider the simple square pattern:

00
01

This pattern can be iterated in two dimensions with the convention that every iteration will consist in adding in line with any pattern thus formed, two identical patterns to the right of and below the original pattern respectively, and completing the square with a fourth pattern formed by interchanging the zeros (0) and ones (1) of the original pattern. Performing this operation three times on the pattern 00 01 yields, successively:

CHART III

00	0000	0000	0000		
01	0101	0101	0101		
	0011	0011	0011		
	0110	0110	0110		
		0000	1111		
		0101	1010		
		0011	1100		
		0110	1001		
		0000	0000	0000	0000
		0101	0101	0101	0101
		0011	0011	0011	0011
		0110	0110	0110	0110

0000	1111	0000	1111
0101	1010	0101	1010
0011	1100	0011	1100
0110	1001	0110	1001
0000	0000	1111	1111
0101	0101	1010	1010
0011	0011	1100	1100
0110	0110	1001	1001
0000	1111	1111	0000
0101	1010	1010	0101
0011	1100	1100	0011
0110	1001	1001	0110

It will be immediately recognised that if the first and fifth rows in the third of the four patterns just written are suppressed, the remainder of said pattern is a replica of the rectangular pattern given in Chart I to represent schematically the slot pattern of Fig. 2, and it can also be verified that if the first and ninth rows of the fourth pattern are suppressed, the remaining rows form another pattern which in principle is suitable for use in an embodiment of the invention employing (up to) fourteen inlet slots and fourteen outlet slots, and patterns suitable for any desired greater number of slots may be obtained in a manner which will now be obvious. Similarly the manner in which the pattern of the second disc is developed from that of the first disc will be obvious.

In what has preceded, we have assumed the use of a detector of radiation which is more faithful and more quickly responsive than is normally fulfilled in detectors suitable for radiation extending far into infra-red. Any practical system of slit modulation should, therefore, take into account the characteristics of such detectors as can be readily provided. One may, for example, assume that the detector employed, hereinafter called of the kind specified, responds to the fundamental frequency of a square wave having the same period as the period of rotation of the discs, but has a negligible response to the third and higher harmonics of such a square wave. Calculation shows that, for example, the fourth of the patterns above indicated is liable with a detector of the kind specified to produce undesired so-called ghost indications, caused by undesired radiations, and the production of patterns suitable for use with a detector of this kind will therefore now be described.

Consider the simple pattern $\begin{smallmatrix}00\\01\end{smallmatrix}$ and apply to this pattern the following two-dimensional iteration process, by which a pattern of 2^n elements on each side is converted into a pattern of 2^{n+1} elements on each side. The upper left quarter and the upper right quarter of the 2^{n+1} pattern are each a reproduction of the 2^n pattern, while the lower left quarter of the 2^{n+1} pattern is symmetrical to the upper left quarter with respect to the horizontal median line, and the lower right quarter is formed by interchanging the ones (1) and zeros (0) of the 2^n pattern. The first four patterns formed in this manner and starting with the elementary pattern $\begin{smallmatrix}00\\01\end{smallmatrix}$, are shown in the following chart.

CHART IV

00	0000	0000	0000
01	0101	0101	0101
	0110	0110	0110
	0011	0011	0011
		0011	1100
		0110	1001
		0101	1010
		0000	1111

Binary Ordinal Numbers					
0000	0000	0000	0000	0000	0
0001	0101	0101	0101	0101	1
0010	0110	0110	0110	0110	0
0011	0011	0011	0011	0011	0
0100	0011	1100	0011	1100	1
0101	0110	1001	0110	1001	0
0110	0101	1010	0101	1010	0
0111	0000	1111	0000	1111	0
1000	0000	1111	1111	0000	0
1001	0101	1010	1010	0101	0
1010	0110	1001	1001	0110	0
1011	0011	1100	1100	0011	1
1100	0011	0011	1100	1100	0
1101	0110	0110	1001	1001	0
1110	0101	0101	1010	1010	1
1111	0000	0000	1111	1111	0

To fully satisfy the requirements for use with a detector of the kind specified, a last transformation of the pattern of sixteen is needed, and one of many binary functions suitable for this transformation has been written in the vertical line at the right of the last-written pattern of sixteen (16). The pattern is corrected by means of said binary function in the sense that all rows for which the said binary function is a one (1), have

their ones (1) replaced by zeros (0) and vice versa, whereas the other rows remain unchanged. The pattern thus obtained is shown below as Chart V.

CHART V

0000	0000	0000	0000
1010	1010	1010	1010
0110	0110	0110	0110
0011	0011	0011	0011
1100	0011	1100	0011
0110	1001	0110	1001
0101	1010	0101	1010
0000	1111	0000	1111
0000	1111	1111	0000
0101	1010	1010	0101
0110	1001	1001	0110
1100	0011	0011	1100
0011	0011	1100	1100
0110	0110	1001	1001
1010	1010	0101	0101
0000	0000	1111	1111

The particular binary function chosen in Chart V has been obtained for the upper half of the pattern of sixteen (16) by observing when the last elements of the binary ordinal number of the row are both zeros (0), and by observing also when the second and third elements of said number are both zeros (0), the number one (1) being taken for the value of the odd binary function whenever either event occurs, and the value zero (0) being taken for all other cases, including the case when the last three elements are zero.

The binary function employed must be symmetrical with respect to the horizontal median line, which furnishes the condition that below the median line either the last two elements of the last said number be ones (1) or that the second and third binits of last said numbers be ones (1).

The various arithmetical operations shown above can be carried out by longhand computation and the strips can be cut in the discs by a manual operation in accordance with the patterns thus computed. A more mechanical process can consist of recording the various patterns as holes in a continuous tape which can be fed to an automatic machine for the operation of marking the discs; the same tape being used over and over for cutting many discs. Also, the computation of the various patterns can be made automatically by means of a computer, this last method being preferable when a great many slots must be cut in a disc.

While Fig. 1 illustrates the employment of slits and of discs circularly slotted, it will be apparent that if discs are made with fine slots these slots themselves can constitute the entrance and exit slits, and members 17 and 18 can be dispensed with, provided a mask with a suitable aperture is substituted for one or both of said members in order to restrict the utilised for the surface of the monochromator to that portion of it which is optically satisfactory. Furthermore, while Fig. 1 illustrates the employment of discs of uniform thickness which are self-supporting, it may be practical to reinforce these discs with radial ribs, or to support them with a disc of material which is substantially transparent to the radiation it is desired to analyse. For instance, if it is desired to analyse the infra-red spectrum in the 1 to 15 micron range, these discs can be formed by vapour-depositing a metallic layer on a disc of polished rock salt, and the light-transmitting slots can be formed by removing circular portions of said metallic layer by means of a ruling tool.

When discs with a great many slots are used, of the order of a hundred, I prefer not to space these slots at exactly equal distances apart, but in the case of the optical arrangement illustrated by Fig. 1, I prefer to decrease the spacing of the entrance slots progressively from the edge of disc 27 towards the centre, or to increase progressively the spacing of the exit strips from the edge of disc 28 towards the centre, or to do both, in order to effect a readily calculable correction for the circumstance that a progressively increasing departure from minimum deviation occurs for rays which enter the apparatus at increasingly greater distances from the optical centre.

While the specific dispersing means illustrated in the spectrometer 10 is a prism, it will be clear that other dispersing means such as a ruled grating could also be utilised, without restricting the scope of my invention, and that the curvature introduced by such other dispersing means in the image of a monochromatic bundle of radiation, as well as lack of symmetry similar to that encountered when departing from the condition of minimum deviation in the case of prismatic dispersion, could be equally well calculated and corrected by one versed and skilled in the art. The spectrometric system of concave and flat mirrors, a prism and a Littrow mirror described herein and shown in Fig. 1 is merely illustrative of a radiation analyser apparatus. Any conventional spectrometer for separation of radiation can be adjusted to accommodate the widening of the entrance and exit apertures and the modulations of the radiation in accordance with the present invention. In practice the entrance and exit apertures 17 and 18 may be replaced by one or two simple masks, with the slots of the discs acting simultaneously as entrance and exit slits to select the radiations and as " on " and " off " slits to modulate the radiations. Consequently the discs alone may be inserted in a variety of spectrometers and by adjustment of the

components produce the above-described results.

It will be apparent that the transmission discs described could be replaced by reflexion discs, which could consist of reflecting discs coated by a non-reflecting layer, out of which strips are removed to provide, in effect, reflecting slots.

It will be clear that while my invention belongs to the art of spectrography and spectrophotometry, apparatus based on the principles disclosed may greatly benefit by the use of recent developments in the art of photography. For instance, the employment of so-called Schmidt-type reflective optical systems (i.e. systems employing a concave mirror in conjunction with a correcting plate) in spectrographs, which, at this writing, is just beginning, will offer far larger benefits when these benefits are two-dimensional, as in the case of my invention, than when they amount only to a lengthening of the allowable single slit length, as in the case of conventional spectrographs.

Obviously numerous changes in construction and rearrangement of the parts might be resorted to without departing from the scope of the invention.

What I claim is:

1. A spectrometer comprising a number of entrance slits for respectively admitting a corresponding number of beams of the radiation to be examined, means for spectrally dispersing all said beams of light, an equal number of exit slits, means for re-converging said spectrally dispersed beams into dispersed spectra and projecting radiation of the selected wavelength from each inlet slit through one of said exit slits, whereby the exit slits are respectively co-ordinated to the individual inlet slits, pulse-coding means associated with each inlet slit for distinctively pulse-coding each of said beams, beam-transit-control means associated with each exit slit, said beam control means being pulse-coded in such manner at each exit slit as to permit radiation bearing the pulse code of the corresponding inlet slit to pass at predetermined on-periods while opposing the passage of such radiation during the interlying off-periods, and to allow radiation bearing the pulse code of any other inlet slit to pass in equal amounts in the on and off periods, and means for measuring the difference of the total radiation passing through the exit slits in the on and off periods respectively.

2. A spectrometer as claimed in claim 1, comprising means for periodically interrupting at different rates and/or phases the beams passing respectively through the various inlet slits and co-ordinated means for periodically interrupting the passage of radiation through the various exit slits at different rates and/or phases respectively.

3. A spectrometer as claimed in claim 2, in which the interrupting means comprise two rotary discs arranged in the path of the light adjacent the positions of the inlet and outlet slots respectively and having rings of spaced slots for effecting the pulse-coding of the various beams.

4. A spectrometer as claimed in any preceding claim, in which the codes are so arranged as to substantially eliminate secondary effects of undesired radiation when using a detector of the kind specified.

5. The modification of the spectrometer as claimed in claim 3, in which the inlet slits are replaced by an inlet aperture and/or the exit slots are replaced by an exit aperture, the slots being made sufficiently narrow to obtain the required definition of the spectra of the individual beams.

6. A spectrometer, more particularly for infra-red spectrometry, substantially as described with reference to the accompanying drawing.

Dated this 12th day of January, 1950.

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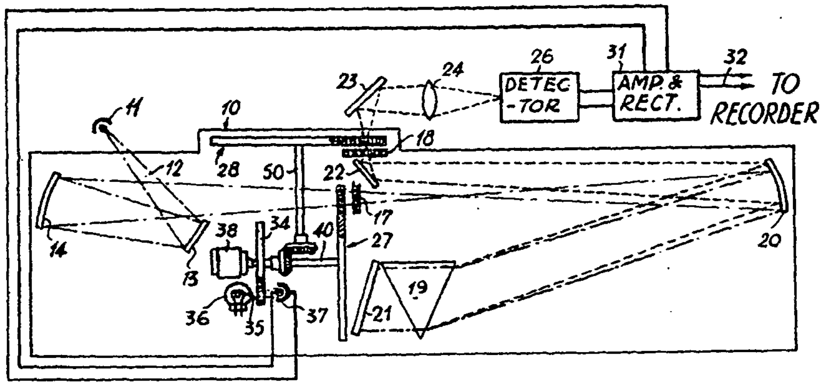

Fig.1.

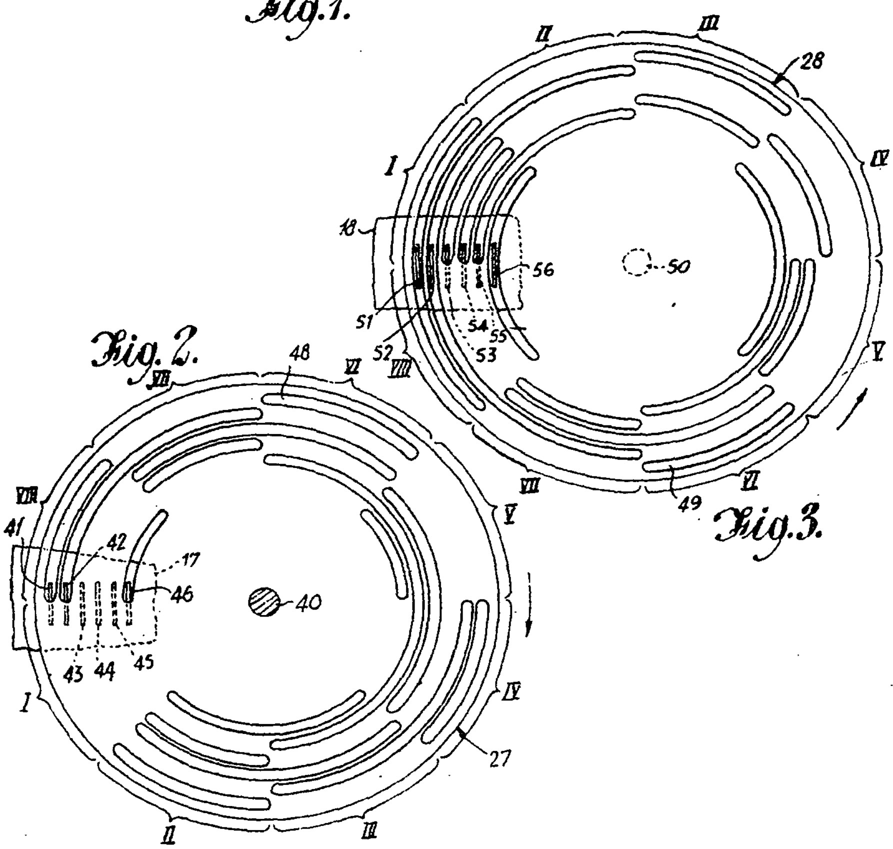

Fig. 2.

Fig. 3.